



High PEMFC performance by applying Ir-V nanoparticles as a cathode catalyst

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ABSTRACT

Very active catalysts Ir-V/C, as a novel suitable cathode catalyst in PEMFCs was synthesized using IrCl_3 and NH_4VO_3 as the Ir and V precursors. By applying the ethylene glycol (EG) method, a well dispersion of Ir-V/C catalysts with mean particle size of 2 nm was obtained. The membrane-electrode assembly (MEA) fabricated with Ir-V nanoparticles exhibited the excellent catalytic activity toward the oxygen reduction reaction (ORR) and, reached 517 mW cm^{-2} at 0.43 V and 210 mW cm^{-2} at 0.30 V in a real fuel cell environment, H_2/O_2 and H_2/air , respectively. In particular, promising results were obtained based on a low metal (Ir) loading of 0.4 mg cm^{-2} on the cathode which achieved 100 h durability at a constant current density of 1200 mA cm^{-2} . The electrocatalytic effect related to a change in the electro-catalyst structure was discussed based on the XRD and TEM data. Also, for the first time, the electrochemical impedance spectra (EIS) and cyclic voltammetry (CV) techniques were used to assess the kinetics of oxygen reduction on the produced samples and the enhancement effect of V in-situ of fuel cells.

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1. Introduction

Replacing platinum as a catalyst has long been an industry goal in proton exchange membrane fuel cells (PEMFCs). Well-known drawbacks of using platinum as a catalyst are its price and scarcity. In particular, the high loading requirements for platinum, especially on the cathode of PEMFCs remains one of the major impediments to commercialize this technology in the automotive industry [1]. Therefore, it is a matter of considerable interest to search for alternative cathode catalysts that are active for oxygen reduction but less expensive. With this consideration, better substitutes for the Pt-free catalysts have been sought after for more than a decade. Several promising candidates were proposed in the past including carbonized catalase [2], Co- or Fe-based catalysts [3], Ru-based alloy catalysts [4,5] pyrolyzed macrocyclic compounds [6] and non-precious metal catalysts [7] in view of their activity as oxygen reduction (ORR). In spite of this progress, very few catalysts showing real promise to comparable Pt in the real H_2/O_2 (air) fuel cell test have been reported so far [8].

With the aim to study potential catalyst candidates that could fill this role, in this communication, a new class of electro-catalyst

consisting of Ir and first-row transition element, V supported on Vulcan XC-72 was synthesized and pursued as a novel cathode catalyst for PEMFCs. Ir is one of the most stable in acid medial among platinum group metals [9] and it is less expensive than Pt [10]. Ir and IrO_x also have been proposed to be as good promoter in Pt/C catalyst because of their excellent oxygen evolution, high activity on CO_{ads} [11] and hydrogen oxidation [12], strong affinity for OH or O species [9]. Most recently, we found that IrCo (M = V, Mn, Fe, Co and Ni) binary alloy catalysts are high active for the hydrogen oxidation reaction after high temperature treatment [13]. Thus, these synthetic catalysts will provide a large potentiality to generate a new function compared to Pt by manipulating the active components in the catalysts. The cost of catalysts could also be lowered much through special design since the synergistic effects are not merely the 'physical' average. As bulk materials, we here demonstrate that V, as a new promoter can significantly enhance the electrocatalytic activity of the Ir site due to a high dispersion of catalyst obtained by applying the polyol process method. Ir-V/C, as the cathode catalyst, thus provides a much better performance in a real H_2/O_2 -air fuel cell.

2. Experimental

2.1. Electro-catalyst preparation

The typical procedure used for the synthesis of Ir-V/C catalysts involved the following steps. 200 mg Vulcan XC-72 carbon, 12 ml

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25 mg ml⁻¹ $\text{IrCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.09 g NH_4VO_3 were added to 50 ml ethylene glycol, ultrasonicated (40 kHz) and stirred for 4 h. Carbon powder (XC-72R) were then added to the mixture, followed by pH adjustment to 12 by the dropwise addition of a 2MNaOH/ethylene glycol solution with vigorous stirring. Extra 20 ml ethylene glycol was added to completely reduce the metal ions and, the solution was left to react at 120 °C for 3 h. The pH of mixture was finally adjusted to 3 by 5 M HCl and cooled down to the room temperature, followed by filtering, washing, and then drying in air at 70 °C. The carbon-supported catalyst powders were then heat-treated at 200 °C in a tube furnace under the mixture gas of N_2 and H_2 (9:1) for 2 h with a flow rate of 600 ml min⁻¹ for N_2 and 70 ml min⁻¹ for H_2 , respectively, to give the final carbon-supported Ir-V catalyst, 40%Ir–10%V/C with a atomic ratio of Ir:V = 1:1.

2.2. Catalyst characterization

Crystal structure identification was performed by XRD (PHILIPS PW 3040/60 powder diffractometer) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 40 mA. A scanning range from 10° to 100° was explored at a scan rate of 1.20 min⁻¹. Particle size was examined by TEM, with a JEM 2010 EX microscope, operating at 200 kV.

2.3. Fabrication of membrane–electrode assembly (MEA)

The catalyst inks were prepared by mixing 40%Ir–10%V/C with a solution of 5 wt.% Nafion (Dupont) and isopropanol, in which the mass ratio of Ir-V/C catalyst to Nafion is 3:1. The catalyst ink was then sprayed directly to the 212 Nafion membrane at 100 °C giving a metal loading of 0.4 mg (Ir) cm⁻². Membrane–electrode assembly (MEA) was prepared by just physically placing gas diffusion layers (GDLs) (Toray TGP-H-090) without the need for a hot-pressing process. For a comparison, the MEA was also fabricated by 40%Ir/C and 40%Pt/C catalyst (Johnson Matthey, JM) on the cathode in the same procedures. The anode adopted the commercial 40%Pt/C catalyst (JM) with Pt loading of 0.4 mg cm⁻² for all the examined electrodes.

2.4. Single cell performance

Catalyst samples were evaluated in a single fuel cell with an active area of 50 cm² in H_2/O_2 –air gas using an electronic load (Sun-Fel200a, Sunrise Power) for discharging and the cell potential was measured under constant current conditions. The cell temperature was 70 °C at 0.1 MPa and the reactant gas streams were humidified through water reservoirs at 75 °C. The flux of H_2 and O_2 were fixed at 500 and 300 ml min⁻¹ (air: 2000 ml min⁻¹), respectively. For a longevity test of the catalyst, a constant current 1200 mA cm⁻² was applied through the cell with H_2 as the anode gas and O_2 as the cathode gas, respectively.

2.5. Kinetic studies in PEMFC

Cyclic voltammetry (CV) measurement was carried out to calculate the electrochemical surface area (ESA) of MEA, where the anode and the cathode were fed with hydrogen and nitrogen, respectively. The anode served as the dynamic hydrogen reference electrode and counter electrode. The polarization curves were obtained in the potential range of 1200 mV down to 50 mV versus the reversible hydrogen electrode (RHE) at a rate of 20 mV s⁻¹. The ESA of the Ir/C and Ir-V/C catalysts were evaluated from CV and a well-reported charge value of hydrogen adsorption/desorption (220 μC) [14].

The electrochemical impedance spectra (EIS) were measured in-situ of the fuel cell where the anode and the cathode were fed

with hydrogen and oxygen, respectively. The anode served as the dynamic hydrogen reference electrode and counter electrode. The spectra were recorded in a frequency range from 10 kHz to 10 mHz using a AC potentiostate (Prinston Instruments) at a current amplitude of 5 A.

3. Results and discussion

Fig. 1 shows the XRD patterns of the C, V/C, Ir/C and Ir-V/C, where the V/C showed characteristic reflections of vanadium. The peak located at 25°, which is the wide graphite (0 0 2) peak, can be assigned to a good graphite characteristic from XC-72 carbon black support. The other peaks correspond to the face-centered cubic (fcc) crystalline of Ir, indicated by the planes of (1 1 1), (2 0 0), (2 2 0), and (3 1 1) at 40.01°, 47.75°, 69.02°, and 85.11°, respectively. After incorporation vanadium, the Ir(1 1 1), Ir(2 0 0) and Ir(2 2 0) peaks in Ir-V/C shifted slightly toward lower angles (higher d spacing) in comparison with those in Ir/C. The very broad Ir(2 2 0) peak in Ir-V/C is consistent with an average particle size around 2 nm calculated from Scherrer formula. These results show that the active components are highly dispersed on the surface of the carbon. The diffraction peaks of Ir or V oxides were not observed in the whole range of XRD patterns. This may be the indicative of dispersion at the atomic level.

In Fig. 2, the dispersion of Ir-V/C and Pt/C catalysts from their TEM images are compared. It can be seen that the metal Ir nanoparticles are uniformly well-distributed on the carbon surface. The corresponding histogram based on the measurements of 200 particles in random regions, revealed that the particle size distribution is rather narrow and have sizes ranged around 2 nm (see inset in Fig. 2(A)). This is much smaller than seen for the conventional commercial Pt/C catalysts, which are on the order of ca. 3–3.5 nm in size (see inset in Fig. 2(B)). Clearly, the modification of Ir with V prevents the Ir particles from aggregation, which contributes to the small particle size. For verifying this effect, TEM images using several Ir-V compositions are presented in Fig. 3. As can be seen, the mean particle size was 1.5–2 nm for 40% Ir/C and narrowly ranged around 2 nm for 40%Ir–10%V/C (Fig. 3(A) and (B)). To our interest, the metal particles in TEM image nearly disappeared for the catalyst sample when the content of V in Ir-V increased to 45% i.e., for 5%Ir–45%V/C (Fig. 3 (D)). Ir-V nanoparticles were ultrafine so that only carbon black particles can be seen covered by in-situ testing support or with an amorphous layer of Ir or Ir-V covered on them. Given a further observation, we can see from Fig. 3(A) that the Ir/C catalyst appeared partly

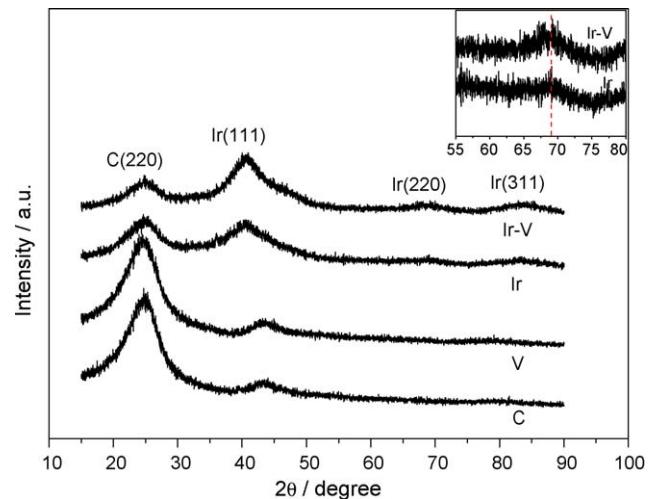


Fig. 1. XRD patterns of 100%C, 20%V/C, 40%Ir/C and 40%Ir-10V%V/C catalyst samples. The inset shows the selected 2θ interval.

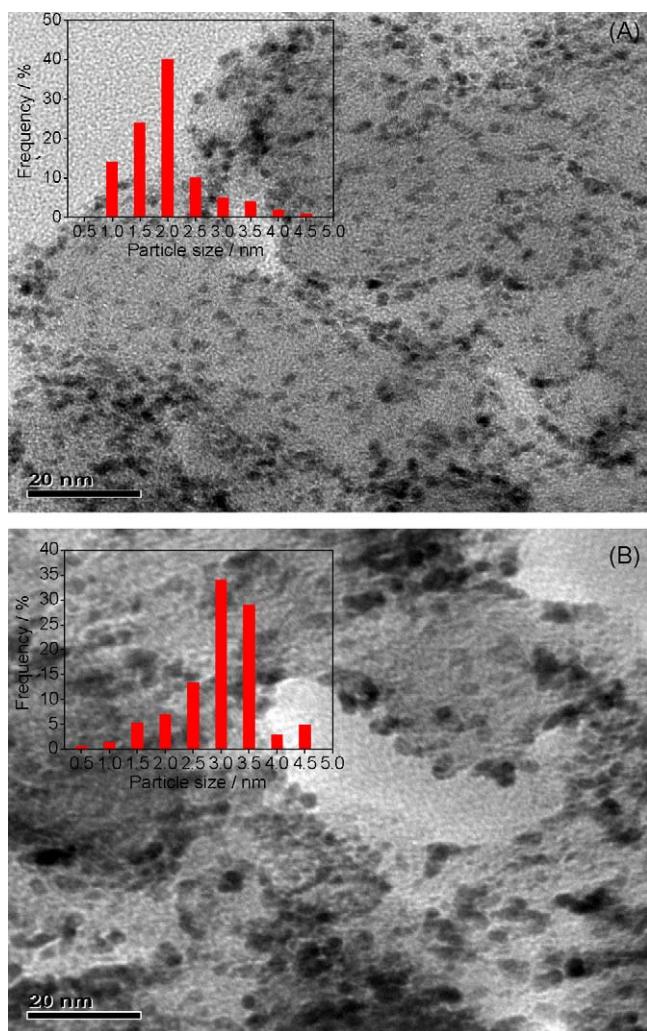


Fig. 2. TEM images of (A) 40%Ir–10V%/ C and (B) 40%Pt/ C (JM) catalysts. The insets show the corresponding particle size distribution of (A) Ir–V/ C and (B) Pt/ C , respectively.

aggregation. However, the Ir–V revealed a good dispersion in the Vulcan XC-72 carbon because of addition of V. This excellent dispersion of the metal nanoparticles may contribute to the high oxygen reduction reaction (ORR) activity of the Ir–V/ C catalyst, which will be discussed in the following sections.

Fig. 4(A) shows single PEMFC performances of Ir/ C , Ir–V/ C and Pt/ C three cathodes with the same platinum anode catalyst in H_2/O_2 conditions. It can be found that Ir–V/ C electro-catalyst showed a very high catalytic activity for the oxygen reduction reaction, especially at high current density range. The power density with Ir–V/ C catalyst reached 517.2 mW cm^{-2} at 1200 mA cm^{-2} , which was even higher than that obtained with Pt/ C under the same experimental conditions (473.4 mW cm^{-2} at 900 mA cm^{-2}). Although the MEA performance fabricated by Ir/ C is inferior, which was just around $1/2$ of Pt/ C , it can be enhanced significantly by the introduction of V. The open circuit voltage (OCV) was also increased from 0.9 V (Ir/ C) to 0.93 V (Ir–V/ C), which is very approaching to Pt/ C in an OCV value of 0.95 V (Table 1).

To investigate the effect of V on the activity of the catalyst, Fig. 5 illustrates the MEA performances for Ir–V/ C cathode catalyst with loading variation (mg cm^{-2}) (different quantities of V) at 5, 10 and 40 wt% of Ir in Ir–V/ C . As the catalyst loading increases, the performance also increased indicating that the more catalyst active sites could be achieved by increasing the catalyst loading. Note, the performances observed in PEMFC are still significant when Ir

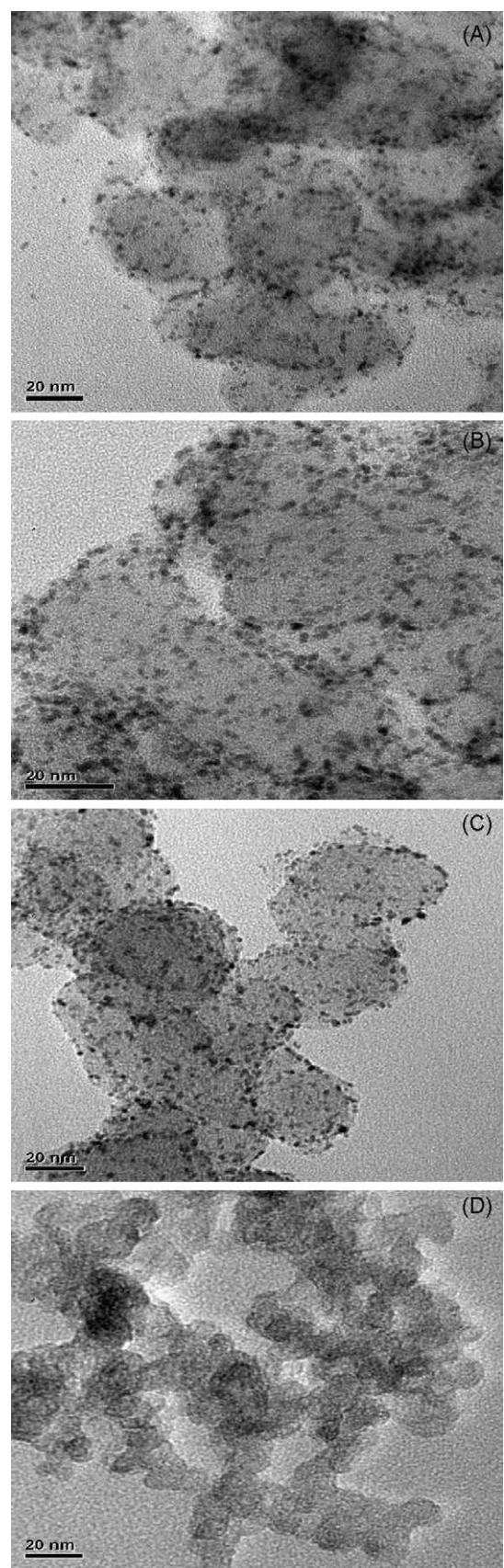


Fig. 3. TEM images of (A) 40%Ir/ C ; (B) 40%Ir–10V%/ C ; (C) 10%Ir–40V%/ C ; and (D) 5%Ir–45V%/ C catalysts, respectively.

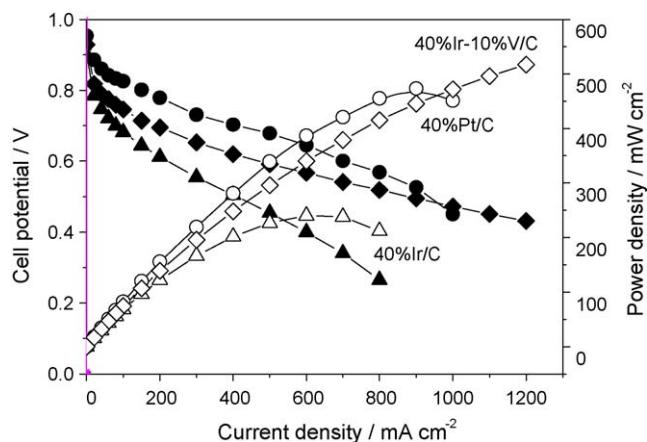


Fig. 4. H_2/O_2 PEMFC polarization curves by applying 40%Ir/C, 40%Ir-10%V/C and 40%Pt/C(JM) as cathode catalysts at 70 °C. Anode: the commercial JM 40% Pt/C catalyst with Pt loading of 0.4 mg cm^{-2} .

amount in the catalyst was reduced to 5%, i.e., 0.1 mg (Ir) cm^{-2} on the cathode, where the kinetic current density at 0.6 V was 1.5 times higher than Ir/C and the maximum power density was 2 times higher than that of Ir/C. As seen in Fig. 3, a different particle size cannot explain this effect since TEM measurements have shown that the mean particle size of Ir/C catalyst is very near to the particle size of Ir-V/C. However, more aggregations were observed in Ir/C than in Ir-V/C. This suggests that the incorporation of V facilitated the high dispersion of Ir on Valuc-X72.

In Fig. 6, the EIS and CV techniques were adopted for the catalytic activity study of Ir/C and Ir-V/C in comparison with Pt/C. By the EIS analysis (Fig. 6(A) and Table 1), one can observe that for Ir/C catalyst, both ohmic resistance and charge transfer resistance for the oxygen reduction in the catalyst layer are very high in comparison with Pt/C catalyst. In contrast, Ir-V/C shows the small charge transfer resistance of oxygen in the catalyst layer in comparison with Pt/C except for a little ohmic resistance improving. By in-situ CV measurement (Fig. 6(B)), the Ir-V/C exhibited a higher electrochemical surface area (EAS, $\text{Se} = 221.05 \text{ m}^2 \text{ mg}^{-1}$) than that of Pt/C ($\text{Se} = 192.17 \text{ m}^2 \text{ mg}^{-1}$), while the Ir/C gave a Se value just around $70.87 \text{ m}^2 \text{ mg}^{-1}$. Clearly, the addition of V significantly improved the dispersion of the metallic components which provides the more effective catalyst sites on the cathode that can take place into the oxygen reduction reactions and thus, a high improved cell performance. It has been reported that the surfaces of Ir have a strong affinity for OH or O species and the formation of Ir-oxide is probably responsible for the low ORR activity [15]. This implies that Vanadium treated catalysts are more resistant against oxidation. This may be attributed to functions of V as oxygen adsorption site and electron bridge. To sum up, the formation of the catalytically active centers should be facilitated by V, although the exact structure of this surface modification has not been identified and a further study is required. Since a combination of Ir with V at a proper Ir:V ratio

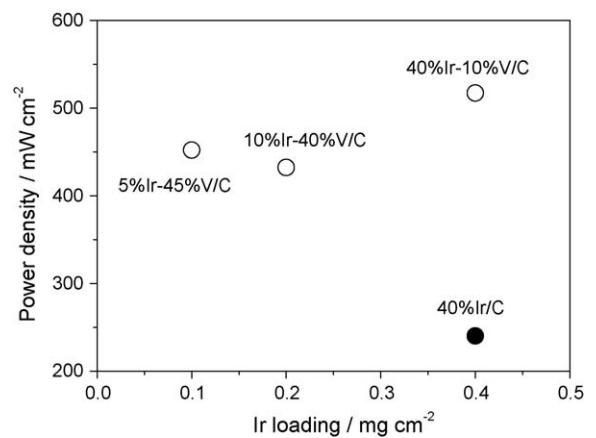


Fig. 5. MEA performances for Ir-V/C cathode catalyst with loading variation, mg (Ir) cm^{-2} at 70 °C. Anode: the commercial JM 40% Pt/C catalyst with Pt loading of 0.4 mg cm^{-2} .

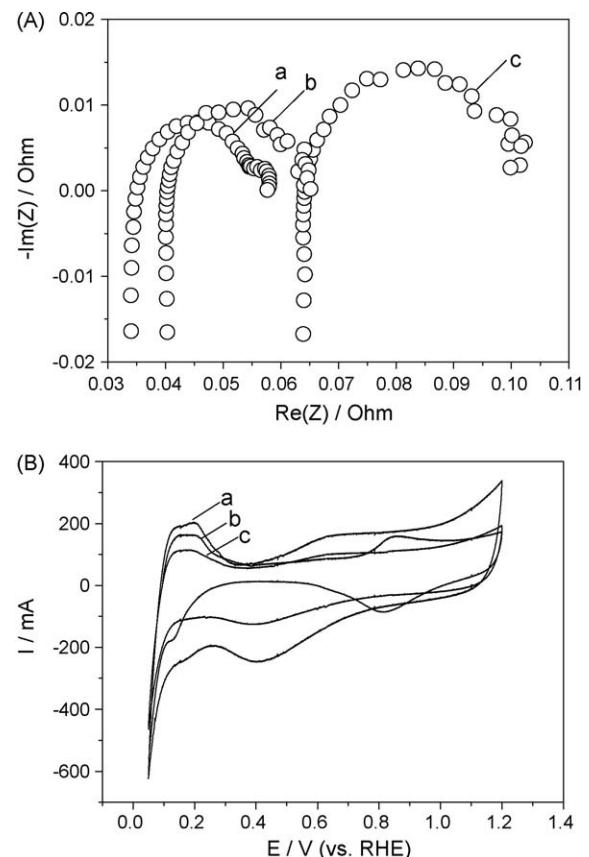


Fig. 6. (A) Electrochemical impedance spectra of (a) 40%Pt/C(JM); (b) 40%Ir-10%V/C; and (c) 40%Ir/C three cathode catalysts at 25 °C; (B) In-situ cyclic voltammetry of (a) 40%Ir-10%V/C; (b) 40%Pt/C(JM) and (c) 40%Ir/C three-cathode catalysts at 25 °C. Anode: the commercial JM 40% Pt/C catalyst with Pt loading of 0.4 mg cm^{-2} .

Table 1

Performance of Ir/C, Ir-V/C and Pt/C cathode catalysts in PEMFC at 75 °C, H_2/O_2 at 0.1 MPa.

Catalyst	OCV (V)	Power density (mW cm^{-2})	Current density (mA cm^{-2})	Cell volatage (V)	R_{HF}^{a} (Ω)	R_{CT}^{a} (Ω)	Se^{b} ($\text{m}^2 \text{ mg}^{-1}$)	Se^{c} ($\text{m}^2 \text{ mg}^{-1}$)
Ir/C	0.90	240.0	600	0.40	0.055	0.042	70.87	–
IrV/C	0.93	517.2	1200	0.43	0.052	0.015	236.47	235.65
Pt/C	0.95	473.4	900	0.53	0.039	0.020	192.17	–

^a Measured by electrochemical impedance spectroscopy (EIS).

^b Measured by cyclic voltammetry (CV) at 0 h.

^c Measured by cyclic voltammetry (CV) after 100 h.

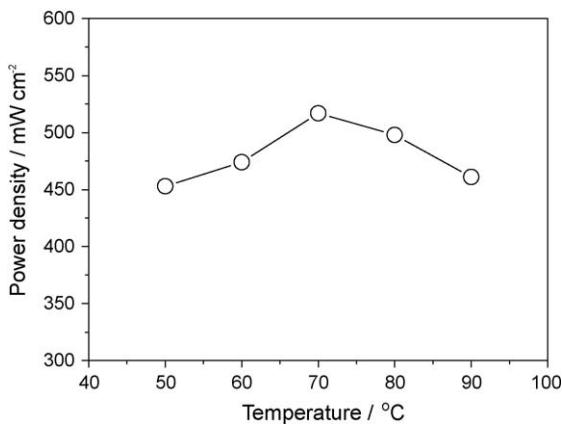


Fig. 7. MEA performances for the best 40%Ir-10%V/C cathode catalyst with temperature variation. Anode: the commercial JM 40% Pt/C catalyst with Pt loading of 0.4 mg cm⁻².

improves the activity significantly towards ORR, compared to Ir alone, in this way, the content of Ir in the catalyst could be reduced much by a special design of the catalyst composed.

The performances of MEA achieved at different temperatures with Ir-V/C as cathode catalyst are shown in Fig. 7. As expected, the performance of the assembly increases as the temperature increase due to increased kinetics. In spite of a low catalyst loading of 0.4 mg (Ir) cm⁻² on the cathode, the MEA gave the good performances that reached power densities of 517 mW cm⁻² at 70 °C and, 474 and 453 mW cm⁻² at 60 and 50 °C, respectively. Further temperature increasing lead to a decrease in the cell performance. These initial results indicated that the Ir-V/C catalyst cell performance could be improved when operated at a reasonable higher temperature.

Fig. 8 shows the MEA performances for Ir-V/C cathode catalyst under a real H₂/air condition. In comparison with Pt/C catalyst under the same operational and experimental conditions, the Ir-V/C performance is about 50% lower than that obtained with platinum. This can be attributed basically to the intrinsic properties of the cathodic reaction of the Ir-based catalyst on the polymeric membrane. The exchange current density of Pt for ORR is 1×10^{-10} A cm⁻² while for Ir is 1×10^{-14} A cm⁻² (in 0.1 M HClO₄). In addition, the composition of air is very different from the case of O₂, therefore, the mass transfer may be largely reduced on Ir-V/C catalyst due to the presence of larger amount of nitrogen where the utilization of oxygen is reduced significantly. However, there are still other options available to test with other transition

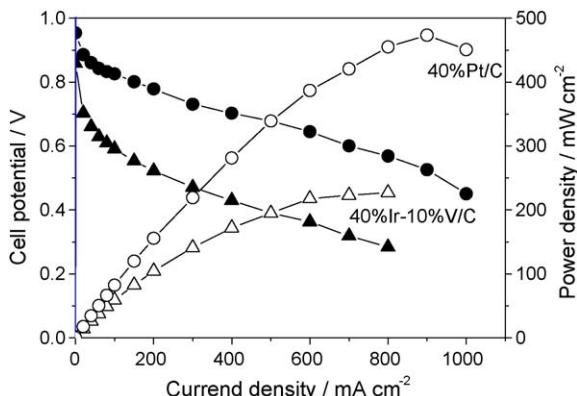


Fig. 8. H₂/air PEMFC polarization curves by applying Ir-V/C and Pt/C as cathode catalysts at 70 °C. Anode: the commercial JM 40% Pt/C catalyst with Pt loading of 0.4 mg cm⁻².

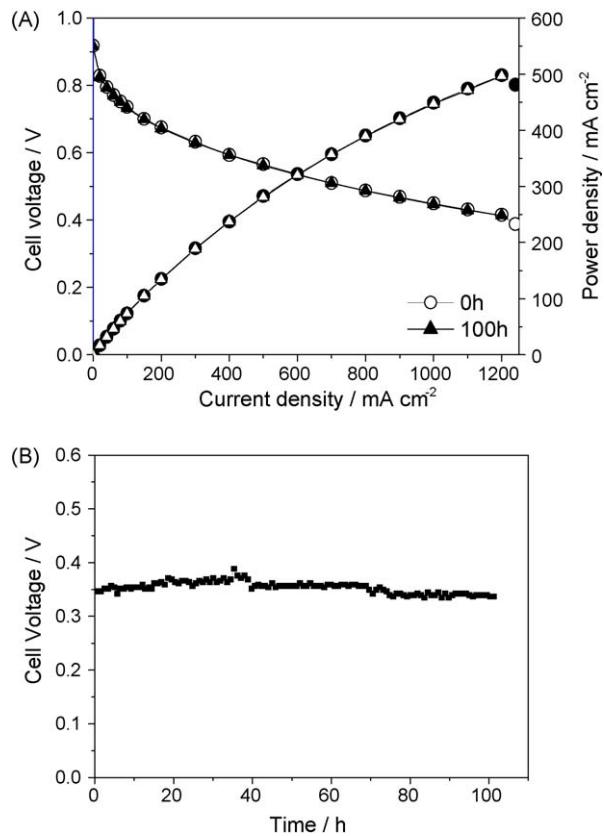


Fig. 9. Variations of (A) polarization curves and (B) cell voltage with operating time by applying Ir-V/C as cathode catalyst in the H₂/O₂ PEMFC at 70 °C.

metals in order to enhance the performance of the iridium-based catalyst or to use significantly more catalyst than the amount required for the initial kinetic activity study.

Longevity of the MEA with 0.4 mg cm⁻² 40%Ir-10%V/C as cathode catalyst was tested in a single fuel cell, where a constant current 1200 mA cm⁻² was applied through the cell with H₂/O₂ gas at 70 °C and 0.1 MPa. The time course of the cell voltage and the power density were tracked during a continuous operation and the results are given in Fig. 9. A striking feature of the initial long-term test is that no appreciable decay of the cell voltage was observed during 100 h continuous operation, and so was the power density (Fig. 8(A)). The cell voltage reached a stable value around 0.37 V (with no iR-corrected voltage) during the whole operation time except for a small undulation due to the cell purging (Fig. 8(B)). It is known that the ESA loss of the catalysts is the main cause of the decay in performance of low temperature PEMFC, which occurs early in the life of a cell. In-situ cyclic voltammetry measurement for MEA showed that the ESA has almost no any change after 100 h life time test due to no loss of catalyst sites on the cathode (Table 1). This implies that Ir-V/C catalyst synthesized in this work may produce a good three-phase boundary at the catalyst layer and at the gas diffusion electrode (GDL)/membrane interface and thus the cell potential keeps constant.

To our knowledge, there have been no works addressing Ir-V/C as cathode catalyst in PEMFC. Only Ir-Sn catalyst in DEFC [16], formic acid oxidation on Pd-Ir catalyst in DFAC [17] and Ir-Se and Ir_xCo_{1-x} methanol tolerance for oxygen reduction [18] have been reported. It is discovered for the first time such a high performance of MEA in both H₂/O₂ and H₂/air conditions, which was fabricated with a cathode of Ir-V/C catalyst. It should be mentioned that several non-platinum alloy for cathode catalysts of PEMFC also have been proposed, particular to Ru-based alloy catalysts.

Nevertheless, their loading on the cathode are very high, exceeding 1.0 mg cm^{-2} [4,5]. In addition, the active area for MEA test are almost 5 cm^2 under the pressure exceeding 2 atm [4,5,19,20]. Comparing the recent outstanding results [8], in this work, very low metal loading of around 0.4 mg cm^{-2} of total Ir catalyst on the cathode with MEA fabricated generated a high performance with a large active area of 50 cm^2 and a long life test of 100 h. This makes Ir-V/C very high potential considering it has no any platinum and the wide variety and applicability of such binary metal components. Further study on the detailed mechanism particular to the promoting effect of V by XPS, EDX, ICP and RRDE and, search for other combinations of active promoters are now under progress.

Acknowledgments

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